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Evidence of Accelerated Thermal Cycling Test Schedules Influencing the Ranking of Zirconia-Base Thermal Barrier Coatings

S.V. Joshi, M.P. Srivastava, and G. Sundararajan

Thermal barrier coatings (TBCs) often encounter temperature cycling in the course of normal operation. In the absence of actual or simulated engine test facilities, accelerated furnace thermal cycling experiments are frequently devised to evaluate the response of various TBCs. This study, which deals with yttria-stabilized and magnesia-stabilized zirconia systems, shows that the performance of a TBC is significantly governed by the severity of the time-temperature schedule employed. More importantly, the ranking of the two zirconia-base TBCs also is influenced by the adopted thermal cycling test schedule. These findings have ramifications in the design of suitable accelerated tests for TBC evaluation.

1. Introduction

PLASMA-SPRAYED zirconia-base thermal barrier coatings (TBCs) have been used for years to improve the material capabilities and service lives of superalloy components for aerospace applications (Ref 1-3). Any candidate ceramic material for TBC systems must possess certain characteristics—particularly a high thermal expansion coefficient that closely matches that of the superalloy substrate and a very low thermal conductivity in order to serve as an effective heat-flux barrier. Zirconia represents the best available compromise between low thermal conductivity (1 to 2 W/m·K) and an acceptable thermal expansion coefficient (9 to 11 × 10^{-6}/K) (Ref 4, 5). However, because of its polymorphic nature, zirconia must be alloyed with other oxides to suppress the disruptive tetragonal-to-monoclinic phase transition and to stabilize the desired tetragonal phase (Ref 5, 6). Yttria, magnesia, calcia, and ceria frequently are used as phase stabilizers. Different degrees of stabilization have been investigated (Ref 7, 8); 6 to 8 wt% yttria-stabilized zirconia (YSZ) and 20 to 25 wt% magnesia-stabilized zirconia (MSZ) are most relevant to the present study. Whereas MSZ has been used for more than 20 years to protect sheet metal combustor components, YSZ represents the current state-of-the-art TBC for gas turbine applications (Ref 9, 10).

Thermal barrier coatings generally encounter temperature cycling in the course of routine operation. Their performance under such demanding conditions primarily governs component durability. The most meaningful nonengine test for TBCs involves temperature cycling in a simulated gas turbine environment offered by a burner rig (Ref 4). However, accelerated furnace thermal cycling tests also are frequently adopted to ascertain the relative merit of various TBCs. These tests may involve cycling between two different furnace temperatures (Ref 11, 12), forced air/inert gas cooling of test specimens from a holding temperature to room temperature (Ref 13, 14), or water quenching of the samples from a holding temperature (Ref 14-16).

Thermal barrier coatings have been the subject of considerable research effort in our laboratory. All furnace thermal cycling studies carried out by the authors to date have involved water quenching of the test specimens from a typical holding temperature of 1200 °C (Ref 17-19). However, a recent study was aimed at evaluating the influence of the accelerated test schedule on TBC performance. The severity of the time-temperature schedule adopted (namely, holding temperature, holding time, cooling rate, etc.) is primarily responsible for the accelerated nature of the furnace cycling tests. This particular study compared test schemes involving water quenching and air cooling, which afford significantly different cooling rates. Initial results show that these factors can have important ramifications in the design of suitable accelerated tests for TBC evaluation.

Keywords: accelerated tests, magnesia-stabilized zirconia, thermal barrier coatings, thermal shock resistance, yttria-stabilized zirconia

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2. Experimental Method

The nickel-base superalloy Nimonic-75, which contains 20% Cr, 0.4% Ti, and 0.1% C, was used as the substrate material throughout the present work. A Ni-20Cr alloy (with a particle-size range of 10 to 53 μm) was employed as the bond coat material. Although it is recognized that the complex MCrAlY alloys (where M is iron, cobalt, nickel, or various combinations therof) constitute the current state-of-the-art bond coats of high-performance TBCs because of their significantly better oxidation/corrosion resistance (Ref 10), nickel-chromium alloys can also be used successfully in actual service provided that the bond coat temperatures remain below 950 °C (Ref 1).

The ceramic overlayers were deposited using either a YSZ powder (with 8 wt% yttria and a particle size range of 5 to 45 μm) or an MSZ powder (with 24 wt% magnesia and a particle size range of 10 to 53 μm). The characteristics of all the spray powders, as well as the spray parameters employed on a METCO Type 7MB plasma spray system (Sulzer Metco Inc.,

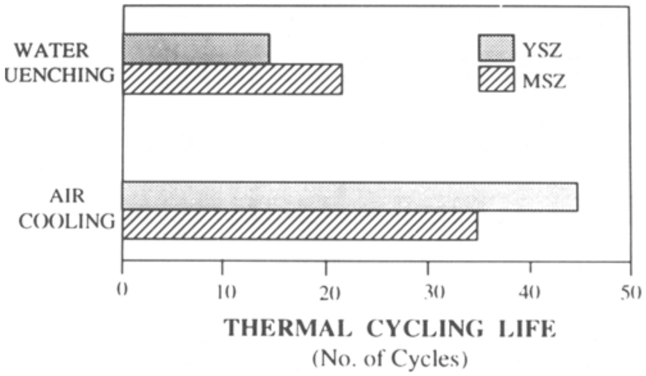

Fig. 1 Relative durability of YSZ and MSZ coatings during thermal cycling tests involving (a) water quenching and (b) natural air cooling to room temperature after 30 min at 1200 °C

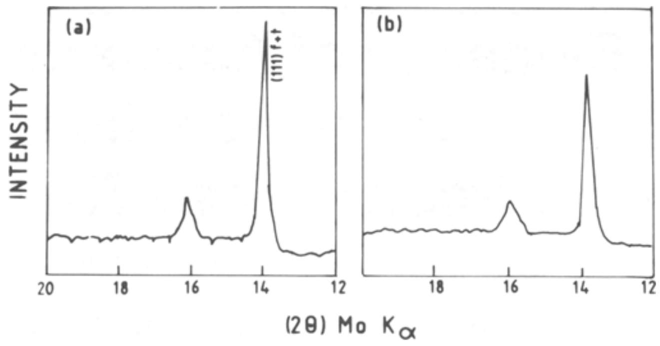

Fig. 2 XRD patterns of plasma-sprayed YSZ coatings. (a) As-coated.(b) After 30 cycles (where each cycle consists of 30 min at 1200 °C followed by natural air cooling to room temperature)

Westbury, NY, USA)to deposit coatings using these powders, are detailed elsewhere (Ref 17, 19).

The TBCs consisted of a bond coat and a ceramic overlayer with respective thicknesses of approximately 100 and 300 μm. For each TBC system, five representative coupons (15 mm by 15 mm) were subjected repeatedly to thermal cycling until coating failure was observed. Each thermal cycle consisted of a 30 min holding at 1200 °C in a furnace, followed by cooling to room temperature either in stagnant air or by water quenching. Comparison of these two cooling methods was the specific objective. Visually detected chipping or debonding of a coated specimen was taken to be the failure criterion for life determination.

A few additional coupons of each coating were also thermally cycled in a similar manner. However, instead of being tested until failure, a coupon was periodically withdrawn after a certain predetermined number of cycles. X-ray diffraction (XRD) analyses of these withdrawn coupons, and of the starting zirconia-base powders and their as-sprayed coatings, monitored the progressive change in phase constitution over the course of thermal cycling. The withdrawn coupons also were examined under a scanning electron microscope (SEM) to determine any change in coating surface texture during thermal cycling.

3. Results and Discussion

Figure 1 shows the comparative durability of YSZ and MSZ thermal barrier coatings under identical thermal cycling conditions. The results reveal that when the specimens are water quenched to room temperature from the holding temperature of 1200 °C, the MSZ coatings endure longer than the YSZ coatings. However, a change in the cooling method from water quenching to natural air cooling reverses this trend.

Figure 1 also indicates that the lives of both YSZ and MSZ coatings were substantially enhanced when the coatings were air cooled rather than water quenched. This observation could be clearly attributed to the reduced severity of the thermal cycle in the former case. The reversal in ranking of the YSZ and MSZ coatings as a consequence of the changed cooling scheme, however, warranted further investigation.

The XRD patterns of as-sprayed YSZ powder coatings as well as coatings subjected to 15 thermal cycles (with water quenching) identical to those adopted here have been previously presented and discussed (Ref 17). The earlier study primarily monitored the monoclinic zirconia phase content in the coatings because any noteworthy contribution to coating failure from zirconia phase transformation is due to the significant volume expansion that accompanies the tetragonal zirconia [(t)-ZrO_2] to monoclinic zirconia [(m)-ZrO_2] transition (Ref 7). No significant change in the monoclinic zirconia phase content occurred during the thermal cycling involving water quenching.

Figure 2 reveals that the same is also true if the YSZ coatings are air cooled during thermal cycling; the XRD patterns of as-coated YSZ specimens and those subjected to 30 thermal cycles are virtually identical. The observation of no apparent change in the phase constitution of YSZ and no evidence of free yttria in either case indicates that the YSZ material is stable under the test conditions employed and that its destabilization has virtually no role to play in the failure of YSZ coatings during temperature cycling.

To ascertain any changes in the phase constitution of the MSZ system, we performed similar XRD analyses of an as-coated specimen as well as two coating specimens subjected to 15 thermal cycles involving both air cooling and water quenching. The XRD patterns (Fig. 3) reveal an increase in both the monoclinic zirconia content and the free-magnesia content (compared to the as-sprayed coating) in the case of the specimen allowed to naturally cool in stagnant air from the holding temperature of 1200 °C during thermal cycling. In contrast, no discernible change in phase constitution occurred in the case of water-quenched specimens; rapid quenching suppresses the changes that otherwise take place under normal cooling conditions.

From the phase diagram for the zirconia-magnesia system (Ref 1), the most likely precipitation scheme on aging cubic zirconia [(c)-ZrO_2] at 1200 °C is

$$\text{(c)-ZrO}_2 \xrightarrow[\text{aging}]{1200\ ^\circ\text{C}} \text{(t)-ZrO}_2 + \text{MgO} \xrightarrow{\text{cool}} \text{(m)-ZrO}_2 + \text{MgO}$$

In the thermal cycling experiments carried out in this laboratory, the specimens were found to cool from the holding temperature

Table 1 Progressive change in constitution of MSZ coatings with thermal cycling

Constituent	Starting powder	As-coated	After 10 cycles	After 15 cycles	After 20 cycles	After 25 cycles
Cubic + tetragonal zirconia	92	92	80	64	53	41
Monoclinic zirconia	...	...	9	21	31	39
Free magnesia	8	8	11	15	16	20

Note: Each cycle consisted of 30 min at 1200 °C followed by air cooling to room temperature.

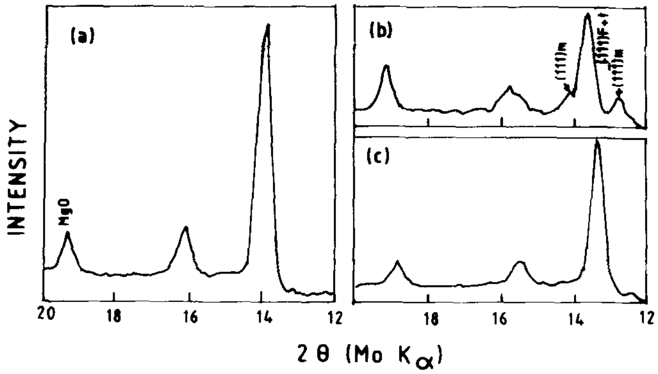

Fig. 3 XRD patterns of plasma-sprayed MSZ coatings. (a) As-coated. (b) After 15 cycles (where each cycle consists of 30 min at 1200 °C followed by natural air cooling to room temperature). (c) After 15 cycles (where each cycle consists of 30 min at 1200 °C followed by water quenching to room temperature)

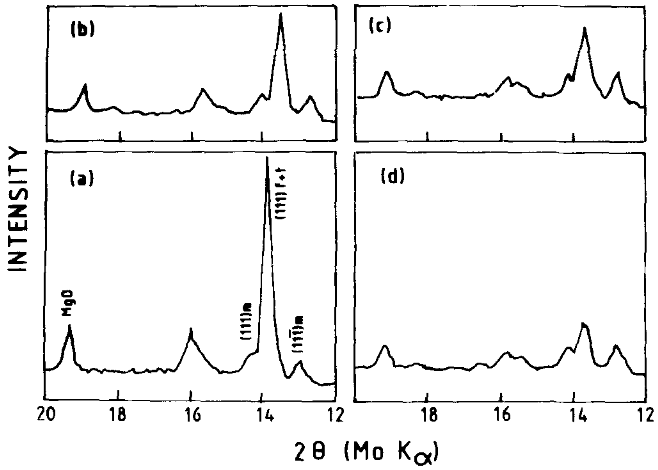

Fig. 4 XRD patterns of plasma-sprayed MSZ coatings during thermal cycling involving natural air cooling (30 min at 1200 °C followed by natural air cooling to room temperature). (a) After 10 cycles. (b) After 15 cycles. (c) After 20 cycles. (d) After 25 cycles

of 1200 °C to room temperature in 15 min, leading to an average cooling rate of close to 80 °C/min. On the other hand, cooling was virtually instantaneous when the same specimens were immersed in a large amount of water. The latter procedure, corresponding to rapid quenching, serves to quench in the tetragonal zirconia phase that may be formed during the aging period. Thus, such an accelerated test conceals the damaging transformation to the monoclinic phase that would normally take place if the specimens were allowed to cool at a normal rate. The XRD results of Fig. 3 corroborate this explanation, which is further reinforced by the results of a more detailed study of the MSZ coatings cooled in natural air from a holding temperature of 1200 °C.

Figure 4 shows the progressive change in XRD patterns of MSZ coatings, determined by analyzing the specimens withdrawn periodically during thermal cycling with air cooling. A gradual increase in the relative intensities of the monoclinic zirconia and free-magnesia peaks is evident. The amounts of the cubic plus tetragonal zirconia phase, the monoclinic zirconia phase, and free magnesia calculated from the peak intensities are given in Table 1.

The progressive precipitation of free magnesia and the transformation of zirconia to the monoclinic form can have damaging consequences. Prominent among these are the considerable volume changes associated with the phase transformation, which can adversely influence coating durability, and increased thermal conductivity, which compromises the insulating effect of TBCs and leads to greater thermal distress in the substrate (Ref 1). These consequences are presumed to be responsible for the decreased durability of MSZ coatings in the more realistic thermal cycling conditions involving air cooling; YSZ coatings undergo no such destabilization. In contrast, in tests involving water quenching, neither YSZ nor MSZ coatings undergo any discernible phase changes during thermal cycling, and their failure can be attributed exclusively to factors such as bond coat oxidation and accumulation of thermal stresses. In this case, the better durability of MSZ coatings is presumably due to the presence in the as-sprayed coatings of some free magnesia, which is known to lead to crack blunting and self-healing of the coatings.

Figure 5 shows SEM photographs of MSZ coatings in the as-sprayed condition and after 10, 20, and 30 thermal cycles. Clearly visible is the progressive coarsening of a precipitate, which is believed to be either magnesia or monoclinic zirconia. No such precipitation was observed in the case of YSZ coatings. This lends further support to the earlier discussion of XRD analyses. A study of the literature has also revealed that competing reactions can indeed lead to precipitation of magnesia and monoclinic zirconia when MSZ is cooled to room temperature after aging at around 1200 °C (Ref 20). Further investigation of the observed precipitates is ongoing, but electron probe microanalysis of these specimens reveals no progressive magnesia segregation (Ref 21).

4. Conclusions

This study provides evidence that the adopted thermal cycling test schedule, particularly the rapidity with which the

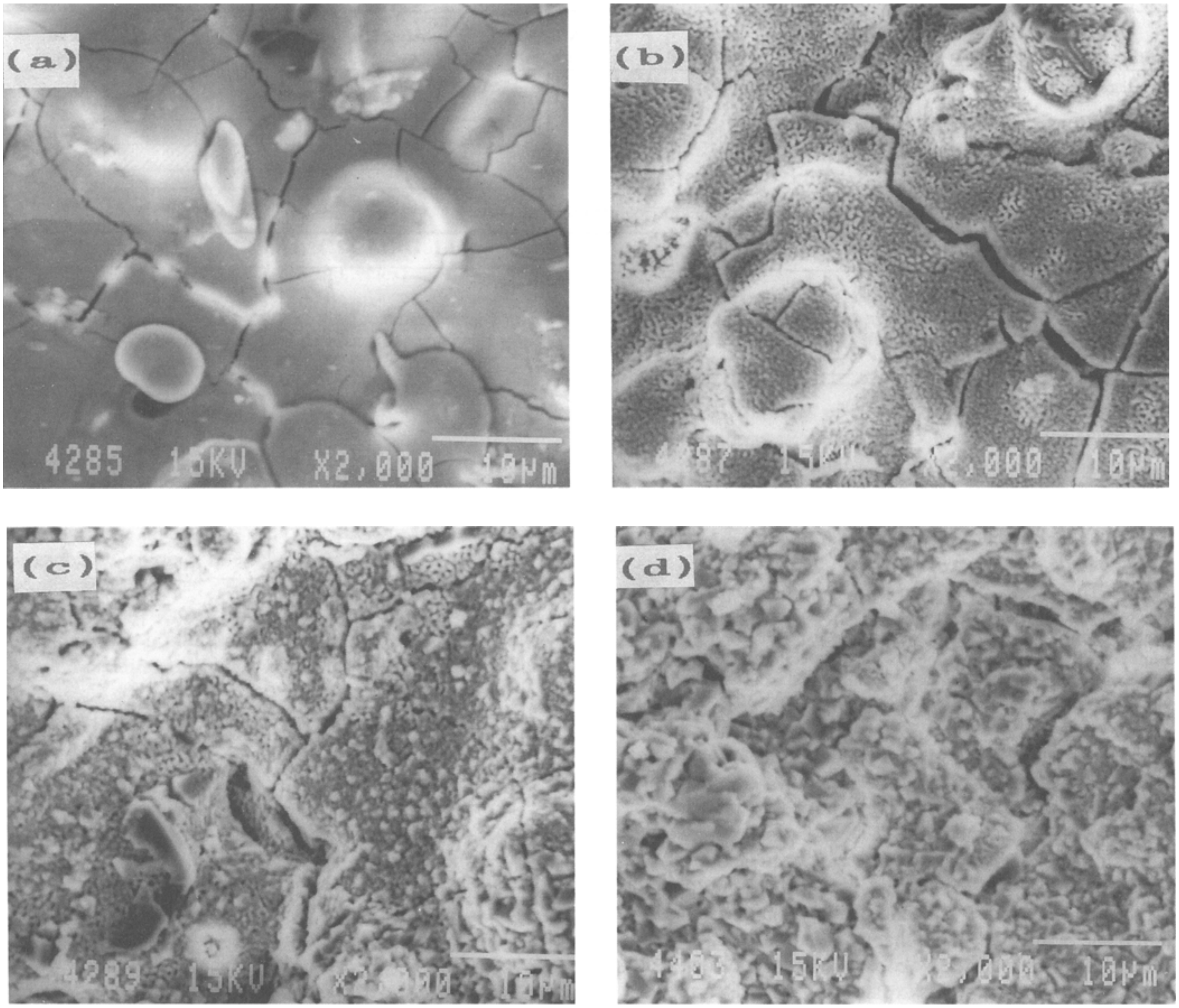

Fig. 5 Topography of MSZ coatings during thermal cycling involving natural air cooling (30 min at 1200 °C followed by natural air cooling to room temperature). (a) After 10 cycles. (b) After 15 cycles. (c) After 20 cycles. (d) After 25 cycles

specimens are cooled from the holding temperature, can influence the ranking of zirconia-base TBCs. Studies of YSZ and MSZ systems revealed the latter to be more durable during thermal cycling involving water quenching to room temperature. However, this trend was reversed when natural air was used for cooling. Investigations suggest that the extremely rapid cooling associated with water quenching can mask the zirconia destabilization that is clearly evident in the more realistic thermal cycling conditions involving air cooling, thereby resulting in a questionable ranking of materials. It has not been ascertained whether such reversal of ranking also occurs in other TBC candidate materials with identical constituent species but compositional variations (e.g., YSZ materials with different yttria contents).

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